Eu^{2+}-doped Ba$_2$CsI$_5$, a new high-performance scintillator

E.D. Bourret-Courchesne [a,*], G. Bizarri [b], R. Borade [b], Z. Yan [a], S.M. Hanrahan [b], G. Gundiah [b], A. Chaudhry [b,c], A. Canning [d], S.E. Derenzo [b]

[a] *Materials Sciences Division of Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Mailstop 55R0121, Berkeley, CA 94720-8119, USA*
[b] *Life Sciences Division of Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*
[c] *Department of Electrical and Computer Engineering, UC Davis, Davis, CA 95616, USA*
[d] *Computational Research Division of Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

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ABSTRACT

The crystal growth and scintillation properties of Ba$_2$CsI$_5$:Eu^{2+} are reported. Crystals were produced by the vertical Bridgman technique in a sealed quartz ampoule. Ba$_2$CsI$_5$:Eu^{2+} presents excellent scintillation properties. An estimated light yield of $97,000 \pm 5,000$ photons per MeV (ph/MeV) of absorbed gamma-ray energy was measured. An energy resolution (FWHM over peak position) of $3.8 \pm 0.3\%$ was observed for the 662 keV full absorption peak. Pulsed X-ray luminescence measurements show a relatively complex time response with four exponential decay components of 48,383, 1500 and 9900 ns with a contribution to the total light output of 1%, 26%, 68% and 25%, respectively. Under X-ray and UV excitation, the emission corresponds to a broadband centered at 2.85 eV. First principles calculations show strong localization of the excited state on the Eu site. Ba$_2$CsI$_5$:Eu^{2+} has a density of about 5 g/cm^3. These first reported scintillation properties make Ba$_2$CsI$_5$:Eu^{2+} a very high-performance scintillator.

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1. Introduction

In the past decades, great effort was made to develop efficient and fast scintillators to detect ionizing radiation. One of the best examples of success is to be found in the development of high performing halide scintillator materials such as cerium activated lanthanum bromide [1] or the recently rediscovered europium activated strontium iodide [2].

Despite outstanding scintillation properties, those materials present a significant challenge for practical applications. For national security applications, economical crystal growth remains one of the dominant criteria of selection. Both materials present properties that make it difficult to scale up from small to large size crystals while keeping a low cost of production. Both are highly hygroscopic and need custom equipment for their crystal growth and handling. Furthermore, LaBr$_3$ crystal growth is challenging due to its propensity to crack during growth. Finally, SrI$_2$ scintillation properties are dependent on europium concentration and crystal size [3]. The search for low production cost crystal is highly desirable.

In this paper, we report the crystal growth of a novel scintillator material, Ba$_2$CsI$_5$:Eu^{2+}. Compared to LaBr$_3$:Ce^{3+} or SrI$_2$:Eu^{2+} scintillators, Ba$_2$CsI$_5$:Eu^{2+} is similar in light output, has an excellent energy resolution below 4%, while being much less hygroscopic. This new scintillator was discovered in an investigation of hundreds of candidates [4].

2. Experimental methods

The crystals were grown from the melt by the vertical Bridgman technique in an evacuated sealed quartz ampoule. The temperature gradient was about 30 °C/cm and the growth rate 1 mm/h. The starting materials were BaI$_2$, CsI and EuI$_2$ (Aldrich). The nominal melt composition had 7% Eu. The segregation of Eu in the crystal is not known at this time and will be measured later. The optimum Eu concentration was determined from high-throughput solid-state synthesis experiments using the facility presented in Ref. [4]. The melting point was estimated to be about 575 ± 25 °C from differential thermal analysis (DTA) experiments in open crucibles under Argon.

The crystal structure determination by the X-ray diffraction was performed on a Siemens SMART-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo Kα, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. The structure was solved by direct methods using SHELX-97 and difference Fourier synthesis [5].

Pulse height spectra were recorded under gamma-ray excitation (^{137}Cs) with a Hamamatsu R6231-100 photomultiplier tube (PMT) connected to an Ortec 113 preamplifier, an Ortec 672

* Corresponding author. Tel.: +1 510 486 6537; fax: +1 510 486 4768.
 E-mail address: EDBourret@lbl.gov (E.D. Bourret-Courchesne).

spectroscopic amplifier and an Ortec EASY-MCA-8K multichannel analyzer. The PMT high voltage was fixed at 650 V. Samples were optically coupled onto the window of the PMT with Viscasil 600,000 (GE) and covered with layers of ultraviolet light reflecting tape (PTFE). All the measurements were done on samples with size ranging from 0.1 to 1 mm^3.

A Nonius FR591 water-cooled rotating copper-anode X-ray generator (50 kV, 60 mA, Bruker AXS Inc., Madison, WI) is used to measure the X-ray excited luminescence. A SpectraPro-2150i spectrometer (Acton Research Corporation, Acton, MA) coupled to a thermoelectrically cooled PIXIS:100B charge coupled detector (CCD) (Princeton Instruments, Inc., Trenton, NJ) was used to measure the X-ray excited emission spectra.

The X-ray excited decay curves were determined on a custom made pulsed X-ray system consisting of an ultrafast laser (200 fs pulses at 165 kHz), a light-excited X-ray tube, a Hamamatsu R3809U-50 microchannel PMT, and an Ortec 9308 picosecond time analyzer [4,6]. The impulse response of the system is 100 ps FWHM.

3. Results

3.1. Crystal characteristics

A photograph of the obtained crystal is shown in Fig. 1. The crystal was found to be clear after removal from the ampoule. The yellow coloration was confined to the crystal/ampoule interface and attributed to iodine segregation. It was also found to have several large grains. Clear small single-crystal pieces were used for the measurements.

Ba$_2$CsI$_5$:Eu was determined to have a monoclinic P2$_1$/c space group with cell parameters a=10.541(3) Å, b=9.256(3) Å, c=14.637(5) Å; β=90.194(6). The structure is the NH$_4$Pb$_2$Cl$_5$ [7] type of structure (Fig. 2), similar to related halides such as CsBa$_2$Br$_5$ [8] and CsEu$_2$I$_5$ [9]. There are two crystallographically inequivalent sites for Ba:Ba1 which is coordinated by seven iodides and Ba$_2$ coordinated by eight iodides (Fig. 2(b) and (c)). The dopant Eu was found to replace Ba1 with attempts to refine the structure with Eu on the Ba$_2$ site being unsuccessful. The amount of Eu was found to be 9% ($\pm$2%), within range of the 7% added to the melt as segregation is expected during crystal growth.

The density, calculated from the structure, is 5.04 g/cm^3 and was measured to be 4.8$\pm$0.2 g/cm^3. It is interesting to note that the crystal is much less hygroscopic than SrI$_2$:Eu^{2+} as judged qualitatively from handling the crystals in the laboratory. More quantitative measurements are underway and will be published later.
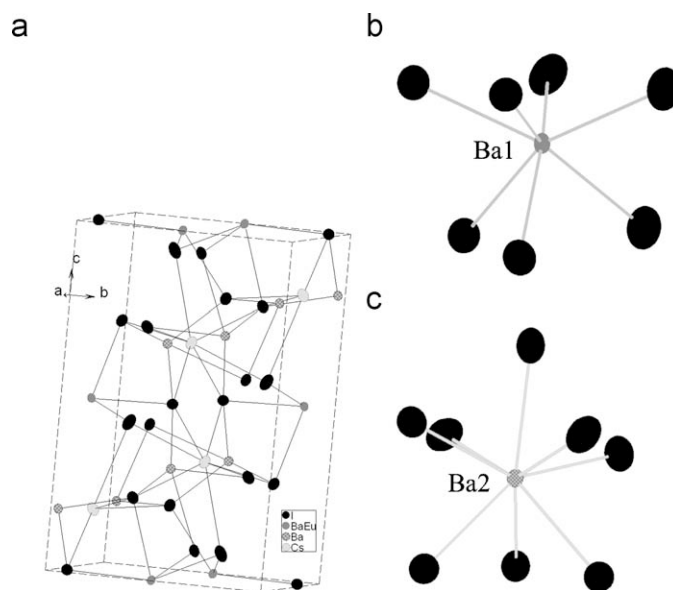

Fig. 2. Representation of the P2$_1$/C-type structure (a) containing two Ba sites of different coordination: Ba$_1$, coordinated by 7 Γ (b) and Ba$_2$ coordinated by 8 Γ (c).

3.2. Scintillation characterization

Fig. 3 shows pulse height spectra for Ba$_2$CsI$_5$:Eu^{2+} and NaI:Tl (St. Gobain) under ^{137}Cs irradiation and amplifier shaping time of 10 μs. To determine the photopeak position and the energy resolution of crystals, part of the photopeak was fitted by Gaussian curves. For Ba$_2$CsI$_5$:Eu^{2+} the photopeak is accompanied by satellite peaks at lower energy due to escape of the characteristics K$_\alpha$, K$_\beta$ X-rays of Ba.

The light output was estimated by comparing the response of NaI:Tl to that of Ba$_2$CsI$_5$:Eu^{2+}. From the fitting, a light output of 97,000$\pm$5000 photons per MeV was estimated for Ba$_2$CsI$_5$:Eu^{2+}, corresponding to 2.2 times the light output of NaI:Tl commonly reported between 43,000 and 45,000 ph/MeV [10,11]. This result puts Ba$_2$CsI$_5$:Eu^{2+} among the best inorganic scintillators in terms of light output. To the authors knowledge, only two other compounds have been reported with a light output higher than 90,000 ph/MeV, cerium activated, LuI$_3$:Ce^{3+}, and europium doped, SrI$_2$:Eu^{2+}. The light output has been estimated between 98,000 and 115,000 ph/MeV [12,13] and between 90,000 and 120,000 ph/MeV [2,14] for LuI$_3$:Ce^{3+} and SrI$_2$:Eu^{2+}, respectively.

The energy resolution, defined as full width half maximum (FWHM) of the 662 keV full absorption peak, is also excellent. A value of 3.8$\pm$0.3% was measured. This energy resolution is among the best results obtained for inorganic scintillators. Only five other crystals have been reported with an energy resolution less than 4% [15]. Furthermore, it can be reasonably expected that Ba$_2$CsI$_5$:Eu^{2+} energy resolution will improve with crystal quality as it has been shown for the majority of scintillators. For instance the first reported values for SrI$_2$ energy resolution was 3.7% [2] for a currently accepted value below 3% [14].

Table 1 and Fig. 4 give estimated light outputs as a function of the shaping time. Estimates were obtained by comparing the photopeak position of our crystal and of a NaI:Tl crystal measured under the same conditions. The results show an increase of the light output with the increase of the shaping time. The maximum light output is measured with a shaping time of 10 μs. The limited shaping time range of our set-up did not allow us to determine whether the integration of the number of photons emitted was complete at 10 μs.
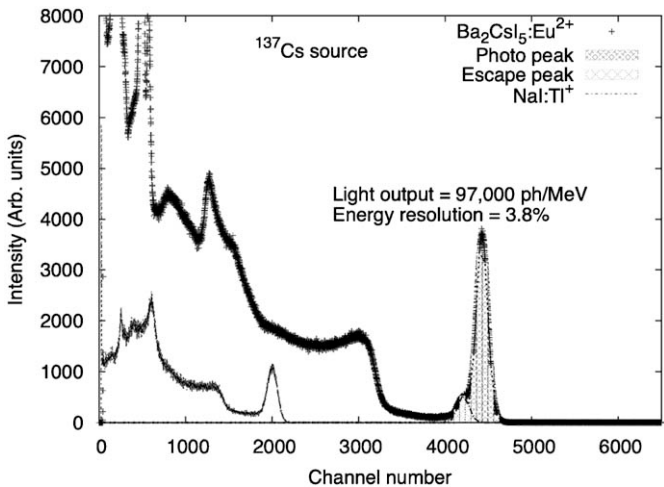

Fig. 1. A 1 cm in diameter Ba$_2$CsI$_5$:Eu^{2+} shown as-grown in a sealed quartz ampoule.

Fig. 3. Pulse height spectra of $Ba_2CsI_5:Eu^{2+}$ and NaI:Tl measured under ^{137}Cs gamma-ray excitation.

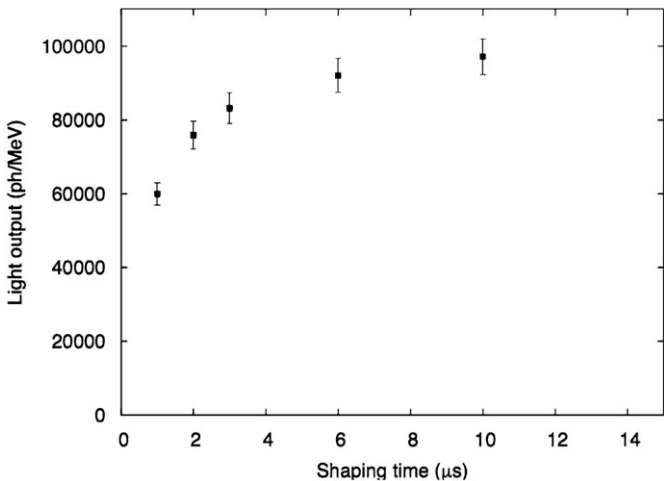Fig. 5. Pulsed X-ray decay curve of $Ba_2CsI_5:Eu^{2+}$ at room temperature.

Table 1
Light yield derived from pulse height spectra of $Ba_2CsI_5:Eu^{2+}$ under 662 keV gamma ray excitation for various shaping times. The energy resolution was recorded with a shaping time of 10 μs at the 662 keV photopeak.

Estimated light yield (10^3 ph/MeV)					Energy resolution
1 μs	2 μs	3 μs	6 μs	10 μs	(%)
61 ± 3	75 ± 3	82 ± 4	90 ± 4	97 ± 5	3.8

Table 2
Lifetimes and contribution to the total light output for each exponential decay component.

Component	Lifetime (ns)	Contribution to the total light (%)
1	48	1
2	383	6
3	1500	68
4	9900	25

Fig. 4. Light yield derived from pulse height spectra of $Ba_2CsI_5:Eu^{2+}$ under 662 keV gamma-ray excitation for various shaping times.
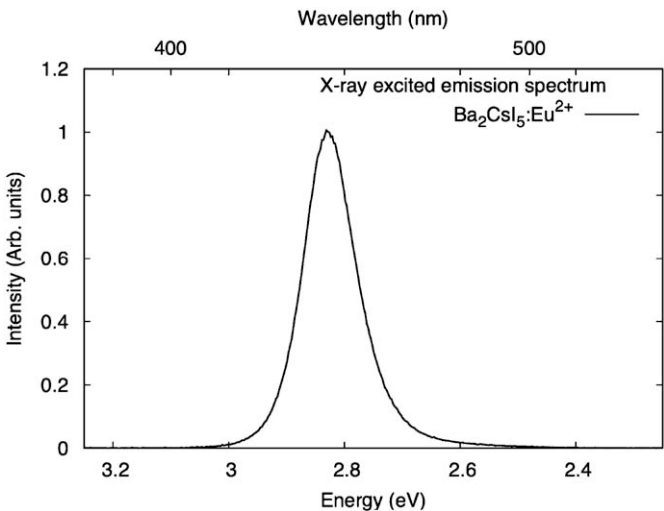
Fig. 6. Normalized X-ray excited emission spectrum of $Ba_2CsI_5:Eu^{2+}$ at room temperature.

Fig. 5 shows the X-ray excited decay curve of $Ba_2CsI_5:Eu^{2+}$. As expected from the shaping time dependence of the light output, $Ba_2CsI_5:Eu^{2+}$ time response extends into the microsecond domain. The decay curve is relatively complex. It corresponds to four single exponential components with lifetimes of 48 ± 5, 383 ± 10, 1500 ± 50 and 9900 ± 100 ns. The contributions to the total light output are 1%, 6%, 68% and 25% for the first, second, third and fourth component, respectively (Table 2). The rise time is less than 1 ns.

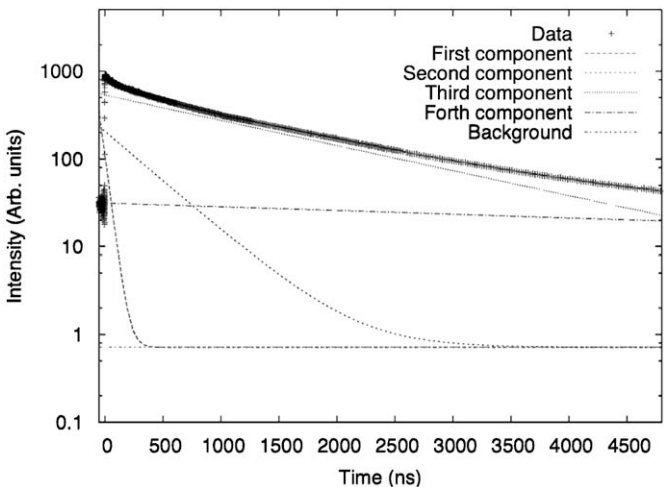The number of components in $Ba_2CsI_5:Eu^{2+}$ time response cannot be explained only by the presence of two Ba substitution sites for the divalent europium. More likely the different components rise from several energy transfer mechanisms with different time responses leading all to the excitation of europium ions. Energy transfer involving self-trapped excitons and self-trapped holes are commonly observed in halide compounds [16,17].

This hypothesis is strengthened by the analysis of the X-ray excited emission spectrum of $Ba_2CsI_5:Eu^{2+}$. The spectrum measured at room temperature is shown in Fig. 6. The spectral shapes
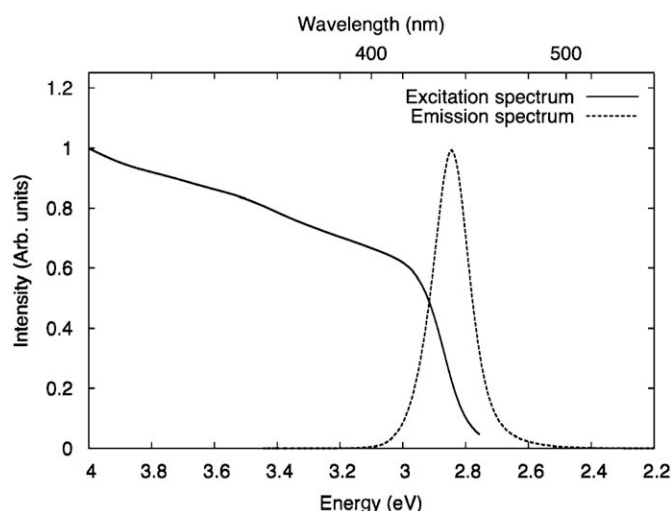
Fig. 7. Normalized excitation (a) and emission (b) spectra of Ba_2CsI_5:Eu^{2+} at room temperature.

are not corrected for the grating efficiency and the photo detector quantum efficiency. The emission spectrum presents a single broadband emission from 3.1 to 2.5 eV with a maximum at 2.85 eV. The emission is characteristic of a divalent europium 5d–4f transition. No additional emitting centers were detected in agreement with the hypothesis that all the energy is transferred to the europium ions.

3.3. Optical characterization

Fig. 7 presents the optical excited emission spectrum of Ba_2CsI_5:Eu^{2+}. The spectrum was measured under 4.1 eV excitation. The emission is identical to the one observed under X-ray excitation; divalent europium 5d–4f transition.

The excitation spectrum, with emission fixed at 2.75 eV, shows a broadband slowly decreasing in intensity from 4 to 3 eV (Fig. 7). The overlap between the excitation and emission spectra indicates that the scintillator might undergo self-absorption as observed in other divalent europium doped compounds [11]. Larger crystals are being studied to determine the impact of the self-absorption on the scintillation properties.

4. First principles calculations

First principles calculations of Eu-doped Ba_2CsI_5 were carried out using the generalized gradient approximation to density functional theory as implemented in the VASP code [18,19] using PAW pseudopotentials [20]. An on-site correction for the Eu 4f electrons was applied using the LSDA+U implementation of Dudarev et al. [21].

The main goal of this calculation is to show that there is a localized excited state of Eu 5d character below the host conduction band. This indicates that a 5d–4f transition is very likely to occur assuming the energy transfer mechanism from the host to the Eu site is efficient.

Fig. 8 shows the calculated iso-surface of electron density for the $(Eu^{2+})^*$ ($[Xe]4f^65d^1$) state. Details of the approach for excited state calculations of Ce doped systems were presented in Ref. [22]. Fig. 8 shows that the excited state is extremely localized on the Eu site, is of 5d character and lies below the conduction band of the host material favoring a 5d–4f type transition. Ground state
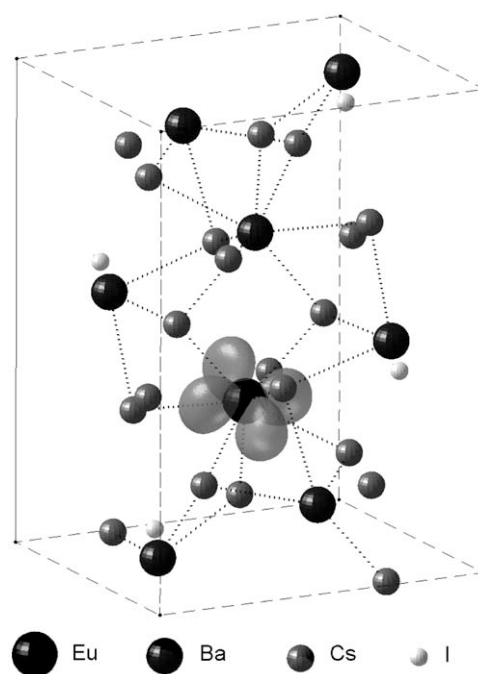

Fig. 8. Iso-surface of the electron density for the $(Eu^{2+})^*$ excited state of Ba_2CsI_5:Eu^{2+} showing strong localization on the Eu atom.

calculations for this system showed the Eu 4f levels to be above the valence band of the host.

5. Conclusion

We present crystal growth and scintillation properties of a new scintillator, Ba_2CsI_5:Eu^{2+}. The crystals were grown by the Bridgman technique in a sealed evacuated quartz ampoule. The scintillation properties are extremely interesting. The results show that Ba_2CsI_5 is activated efficiently with Eu^{2+}. The light output under ^{137}Cs excitation is estimated to be 97,000 photons per MeV. While the scintillation light is slower than that produced from Ce^{3+} activation, most of the light is emitted within 1500 ns, it is still fast enough for applications related to national security. Its energy resolution, defined as full width half maximum (FWHM) of the 662 keV full absorption peak, is 3.8%. Its density was calculated from the structure to be 5.04 g/cm^3 and measured to be 4.8 g/cm^3.

Compared with SrI_2:Eu^{2+}, the light output and time response are in the same order of magnitude. The energy resolution is slightly higher than the 3% measured for SrI_2:Eu^{2+} [14] but comparable to the first value reported for this material [2]. The density is higher and Ba_2CsI_5:Eu^{2+} appears to be less hygroscopic than SrI_2:Eu^{2+}. These initial results are very promising considering that the crystal quality can still be improved and optimized.

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